SECOND EDITION

CARBON DIOXIDE THERMODYNAMIC PROPERTIES HANDBOOK

Covering Temperatures from -20° to 250°C
and Pressures up to 1000 bar

Sarah Anwar and John J. Carroll

Scrivener
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Carbon Dioxide Thermodynamic Properties Handbook

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Sara dedicates this book to her parents, Anwar Alam and Arjumand Bano.

In addition both authors would like to dedicate this book to their co-workers at Gas Liquids Engineering.

Contents

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Preface to Second Edition

As we move towards a carbon-free society, the properties of carbon dioxide remain important for the optimum design of processes for dealing with CO_2. In the pursuit of such a goal the properties of CO_2 are important to many fields including engineering, geology, and chemistry. Of course, carbon dioxide is an important chemical merely from a scientific point of view and again these tables are useful for obtaining a fuller understanding of its behavior.

The second edition of the book has expanded front matter and an added appendix but the tables themselves remain unchanged.

Preface to First Edition

Next to water, carbon dioxide is probably one of the most studied substances in the annals of science. It has a readily accessible critical point (30.98 °C and 73.77 bar) which makes it interesting to study in the lab. Furthermore it is relative safe (compared with hydrocarbons and toxic chemicals such as hydrogen sulfide). The measurements have been critically reviewed and complex, highly accurate equations of state have been developed.

In the 21^{st} Century carbon dioxide has become an important social chemical. It has been implicated in the global climate change. Governments are scrambling to deal with emissions of CO_2 to the environment, including taxing emitters. Carbon dioxide may one day rival other commodities.

This is the most comprehensive collection of data on the thermodynamic properties of carbon dioxide ever published, and much of this information is now no longer available in such a ready format anywhere else. The authors hope that this volume will become the standard reference work for engineers, chemists, and scientists everywhere, who are studying, working with, or hoping to combat carbon dioxide.

Introduction

Presented in this book are tabulated properties for pure carbon dioxide. The properties are based on the equation of state of Span and Wagner (1996). Although Span and Wagner (1996) also included tabular properties, their values are at courser intervals and thus are a little difficult to use directly. The properties given here are at fine intervals of temperature and pressure and make rapid interpretation much easier.

The range of temperatures and pressure was selected as being appropriate for the application of carbon dioxide sequestration. However, the tabulated data are not limited to that application.

The first tables in this book are for the properties of saturated carbon dioxide. Thus the pressures given in these tables are the vapor pressure of pure CO_2 and they end at the critical point. One thing that looks unusual is that the heat capacity, C_p, is infinite at the critical point. However, this is true by definition. Subsequent tables are for the density, enthalpy, entropy and heat capacity for vapor, liquid and supercritical regions.

Derived Properties

From the tables provided in this book several other properties can be calculated directly. This section provides the formulae to perform these calculations.

Molar Volume

The molar volume, v, is basically the reciprocal of the density and can be calculated using the following definition:

$$v = \frac{M}{\rho} \tag{1}$$

where: v is the molar volume, m^3/kmol
M is the molar mass of carbon dioxide, 44.010 kg/kmol
ρ is the density, kg/m^3

Compressibility Factor

The compressibility factor, z, can be calculated from the values in the density tables using the following definition:

$$z = \frac{M\,P}{\rho\;R\;\left(t + 273.15\right)} \tag{2}$$

where: z is the compressibility factor, dimensionless
M is the molar mass of carbon dioxide, 44.010 kg/kmol
P is the total pressure, bar
ρ is the density, kg/m^3
R is the universal gas constant, 0.083 145 bar·m^3/kmol·K
t is the temperature, °C

Specific Properties

The tabulated values for the enthalpy, entropy, and heat capacity are on a molar basis. In order to convert them to the specific property (per unit mass), divide by the molar mass of carbon dioxide (44.010 g/mol).

$$H = h/M$$

where: H is the specific enthalpy, kJ/kg
h is the molar enthalpy, kJ/kmol (or J/mol)
M is the molar mass of carbon dioxide, 44.010 kg/kmol

$$S = s/M$$

where: S is the specific entropy, kJ/kg·K
s is the molar entropy, kJ/kmol·K (or J/mol·K)
M is the molar mass of carbon dioxide, 44.010 kg/kmol

$$C_p = \mathrm{C_p}/M$$

where: C_p is the specific heat capacity, kJ/kg·K
$\mathrm{C_p}$ is the molar heat capacity, kJ/kmol·K (or J/mol·K)
M is the molar mass of carbon dioxide, 44.010 kg/kmol

Internal Energy

The internal energy, U, in kJ/kg can be calculated the following definition:

$$U = H - \frac{100\,P}{\rho} \tag{3}$$

where: U is the specific internal energy, kJ/kg
H is the specific enthalpy, kJ/kg
P is the pressure, bar
ρ is the density, kg/m^3

Alternatively, the molar internal energy, u, in J/mol can be calculated from:

$$u = h - \frac{100\,M\,P}{\rho} \tag{4}$$

where: u is the molar internal energy, J/mol
M is the molar mass of carbon dioxide, 44.010 kg/kmol
h is the molar enthalpy, J/mol

Linear Interpolation

The tables provided are at fine grids of temperature and pressure. However, for more accurate calculations the tables should be interpolated. The grid is sufficiently fine that linear interpolation is satisfactory.

$$y = \left(\frac{y_1 - y_2}{x_1 - x_2}\right)(x - x_1) + y_1 \tag{5}$$

One must be careful not to interpolate across the vapor pressure.

Example 1

What is the enthalpy of carbon dioxide at 50 °C and 6.25 bar?

Answer: From Table 9 at 50 °C:
P = 6 bar h = 734.0 J/mol (point 1)
P = 7 bar h = 698.4 J/mol (point 2)

Interpolating:

$$\begin{aligned} y &= \left(\frac{734.0-698.4}{6-7}\right)(6.25-6)+734.0 \\ &= \underline{725.1\ \text{J/mol}} \end{aligned}$$

Example 2

What is the enthalpy of carbon dioxide at 71.3 °C and 18 bar.

Answer: From Table 9:

	17.5 bar	20 bar
71 °C	1209.5 J/mol	1127.4 J/mol
72 °C	1252.2 J/mol	1170.8 J/mol

Interpolate with the pressure

$$\begin{aligned} y &= \left(\frac{1209.5-1127.4}{17.5-20}\right)(18-17.5)+1209.5 \\ &= \underline{1193.1\ \text{J/mol}} \end{aligned}$$

and

$$\begin{aligned} y &= \left(\frac{1252.2-1170.8}{17.5-20}\right)(18-17.5)+1252.2 \\ &= \underline{1235.9\ \text{J/mol}} \end{aligned}$$

These interpolations are summarized in the following table:

	17.5 bar	*18 bar*	20 bar
71 °C	1209.5 J/mol	*1193.1 J/mol*	1127.4 J/mol
72 °C	1252.2 J/mol	*1235.9 J/mol*	1170.8 J/mol

Interpolate with the temperature (the italicized values in the above table).

$$\begin{aligned} y &= \left(\frac{1193.1-1235.9}{71-72}\right)(71.3-71)+1193.1 \\ &= \underline{1205.9\ \text{J/mol}} \end{aligned}$$

Sample Calculations

Presented in this section are some sample calculations based on classical thermodynamics, which demonstrate some applications for the tables.

Joule-Thomson Expansion

One of the classic examples in thermodynamics is the expansion of a fluid across a valve (or a porous plug), which is a constant enthalpy process. The process is shown in Figure 1. The specification of this process is given the temperature and the pressure of the inlet (state 1) and the pressure at the outlet (state 2), calculate the temperature of the outlet stream. Since this is an isenthalpic process, we also know that:

$$h_1 = h_2$$

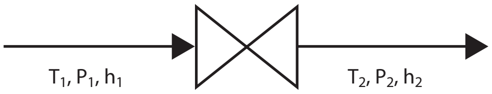

Figure 1 Schematic of the Joule-Thomson Expansion.

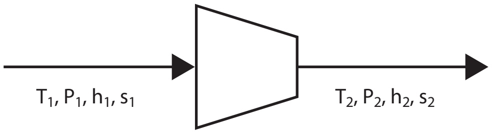

Figure 2 Schematic of the Compression of a Gas Stream.

Isentropic Compression

An ideal compressor is an isentropic process (i.e. the change in entropy of the stream is zero). A simple schematic of a compression process is shown in Figure 2. The specification for a compressor is the inlet temperature and pressure and the outlet pressure (or equivalently the compression ratio). For the ideal case:

$$s_1 = s_2$$

Thus the outlet of the compressor is specified by P_2 and s_2 from which the other properties can be calculated.

The ideal, adiabatic work compression can then be calculated from the difference in the enthalpies:

$$w^* = h_2 - h_1$$

where w^* is the ideal, adiabatic work of compression, J/mol

Tank Filling

Figure 3 shows the schematic for a simple tank filling process. In this case a header is used to fill the tank. The control volume would include the valve and thus the temperature after the valve is not significant to the solution to the problem.

Assuming the tank is initially evacuated, or nearly so, then the first law analysis of this system (Van Wylen and Sonntag, 1985) yields the following equation:

$$m_1 h_1 = m_t u_t$$

The continuity (mass balance) means that the mass of fluid flowing into the tank is equal to the mass of the filled tank, so this equation further reduces to:

$$h_1 = u_t$$

For this simplified tank filling problem, the internal energy in the tank equals the enthalpy of the flowing stream entering the tank. A change in temperature arises because of the difference between enthalpy and internal energy.

Example 3

Calculate the temperature drop when a carbon dioxide stream is throttled from 7 bar and 50 °C to 1 bar.

Answer: At 7 bar and 50 °C the enthalpy is 698.4 J/mol (from Table 6). At 1 bar, from Table 6 we have the following:

Temperature	Enthalpy
44 °C	678.2 J/mol·K
45 °C	716.5 J/mol·K

By linear interpolation:

$$y = \left(\frac{44-45}{678.2-716.5}\right)(698.4-678.2)+44$$
$$= 44.5°\text{C}$$

So the exit temperature is 44.5 °C, a cooling of about 5.5 Celsius degrees.

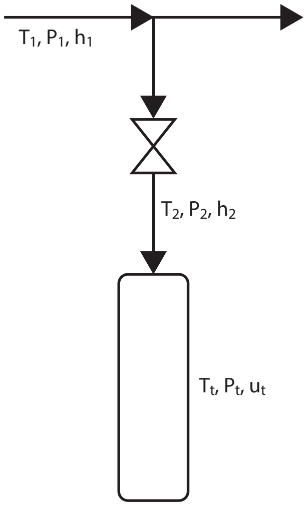

Figure 3 Schematic of the Classic Tank Filling Problem.

Example 4

The suction pressure is 3.5 bar and the temperature is 50 °C. For a discharge pressure is 10 bar calculated the discharge temperature and the work of compression.

Answer: The flowing properties are for carbon dioxide at 50 °C at 3 and 4 bar are from Tables x and y and the value at 3.5 bar is interpolated from these values.

	3 bar	*3.5 bar*	4 bar
entropy	–6.214 J/mol·K	*–7.448 J/mol·K*	–8.682 J/mol·K
enthalpy	839.3 J/mol	*821.9 J/mol*	804.4 J/mol

From Table 11 at 10 bar, it can be seen that the discharge temperature is between 130° and 131 °C, because the entries in the table span the entropy value at 50 °C and 3.5 bar (–7.448 J/mol K). In fact, from these vales it can be seen that the discharge temperature is almost exactly 131 °C. For many cases this may be sufficiently accurate.

However the values for the entropy can be used to interpolate the temperature more accurately as shown below:

	130 °C	*130.99 °C*	131 °C
entropy	–7.583 J/mol·K	*–7.448 J/mol·K*	–7.447 J/mol·K
enthalpy	3916.2 J/mol	*3958.4 J/mol*	3958.8 J/mol

$$
\begin{aligned}
y &= \left(\frac{130-131}{-7.583--7.447}\right)\left(-7.583--7.448\right)+130 \\
&= 130.99^{\circ}\mathrm{C}
\end{aligned}
$$

Finally the ideal, adiabatic work of compression is the change in enthalpy:

$$w^{*} = 3958.4 - 821.9 = \underline{3136.5\ \mathrm{J/mol}}$$

Example 5

If the line pressure is 70 bar and the flowing temperature is 50 °C, what is the temperature of the tank if the filling process is stopped once the tank pressure reaches 50 bar?

The enthalpy of the flowing stream is –2323.4 J/mol thus, the internal energy of the filled tank is –2323.4 J/mol.

Guess a final tank temperature of 75 °C and calculate the internal energy:

$$\begin{aligned}u &= h - \frac{1000\,M\,P}{\rho}\\ &= 256.6 - \frac{(100)(44.010)(50)}{90.93}\\ &= -2394.3\text{ J/mol}\end{aligned}$$

Then try 80 °C and interpolate yields about 76 °C, so estimate the internal energy at 76 °C:

	75 °C	80 °C	76 °C
enthalpy	256.6 J/mol	517.5 J/mol	309.1 J/mol
density	90.93 kg/m³	88.23 kg/m³	90.00 kg/m³
internal energy	–2394.3 J/mol	–1976.5 J/mol	–2135.9 J/mol

So the final temperature is between 75° and 76 °C. Interpolating yields: 75.27 °C. Note the temperature of the tank increases from the filling process.

Conversion Factors

From	**To**	**Multiply by**
kg	lb	2.20462
m³	ft³	35.3147
kg/m³	lb/ft³	0.062428
J/mol	Btu/lb-mol	0.429923
kJ/kg	Btu/lb	0.429923
J/mol·K	Btu/lb-mol·R	0.238846
kJ/kg·K	Btu/lb·R	0.238846
kg/kmol	lb/lb-mol	1
bar	kPa	100
bar	MPa	0.1
bar	atm	0.986923
bar	psia	14.5038

Temperature: t/°F = (t/°C) × 9/5 + 32

–20 °C = –4 °F
–15 °C = +5 °F
–10 °C = 14 °F
–5 °C = 23 °F
0 °C = 32 °F
5 °C = 41 °F
10 °C = 50 °F
15 °C = 59 °F
20 °C = 68 °F
25 °C = 77 °F
30 °C = 86 °F
50 °C = 122 °F

100 °C = 212 °F
150 °C = 302 °F
200 °C = 392 °F
250 °C = 482 °F

0 °F = $-17\tfrac{7}{9}$ °C
50 °F = 10 °C
100 °F = $37\tfrac{7}{9}$ °C
150 °F = $65\tfrac{5}{9}$ °C
200 °F = $93\tfrac{1}{3}$ °C
250 °F = $121\tfrac{1}{9}$ °C
300 °F = $148\tfrac{8}{9}$ °C
350 °F = $176\tfrac{2}{3}$ °C
400 °F = $204\tfrac{4}{9}$ °C
450 °F = $232\tfrac{2}{9}$ °C

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1

Density (kg/m³) of Saturated Carbon Dioxide

Table 1 Density (kg/m³) of Saturated Carbon Dioxide

Temp (°C)	Press (bar)	Liquid	Vapor	Temp (°C)	Press (bar)	Liquid	Vapor
–20	19.70	1031.7	51.70	9	43.92	868.4	130.7
–19	20.31	1027.0	53.40	10	45.02	861.1	135.2
–18	20.94	1022.3	55.15	11	46.15	853.6	139.8
–17	21.58	1017.6	56.96	12	47.30	845.9	144.7
–16	22.24	1012.8	58.82	13	48.47	837.9	149.8
–15	22.91	1008.0	60.73	14	49.66	829.7	155.1
–14	23.59	1003.1	62.70	15	50.87	821.2	160.7
–13	24.29	998.1	64.73	16	52.11	812.4	166.7
–12	25.01	993.1	66.81	17	53.37	803.3	172.9
–11	25.74	988.1	68.97	18	54.65	793.8	179.6
–10	26.49	982.9	71.18	19	55.96	783.8	186.6
–9	27.25	977.7	73.47	20	57.29	773.4	194.2
–8	28.03	972.5	75.83	21	58.65	762.4	202.3
–7	28.82	967.1	78.26	22	60.03	750.8	211.1
–6	29.63	961.7	80.77	22	60.03	750.8	211.1
–5	30.46	956.2	83.36	23	61.44	738.4	220.6
–4	31.30	950.6	86.03	24	62.88	725.0	231.1
–3	32.16	945.0	88.79	25	64.34	710.5	242.7
–2	33.04	939.2	91.65	26	65.84	694.5	255.9
–1	33.94	933.4	94.60	27	67.36	676.4	271.0
0	34.85	927.4	97.65	28	68.92	655.3	289.1
1	35.78	921.4	100.8	29	70.51	629.4	312.0
2	36.73	915.2	104.1	29.5	71.32	613.3	326.6

Table 1 Density (kg/m³) of Saturated Carbon Dioxide (cont.)

Temp (°C)	Press (bar)	Liquid	Vapor	Temp (°C)	Press (bar)	Liquid	Vapor
3	37.70	909.0	107.5	30.0	72.14	593.3	345.1
4	38.69	902.6	111.0	30.2	72.47	583.5	354.3
5	39.70	896.0	114.6	30.4	72.80	572.0	365.3
6	40.72	889.4	118.4	30.6	73.13	557.7	379.1
7	41.77	882.5	122.3	30.8	73.47	537.4	399.2
8	42.83	875.6	126.4	30.98	73.77	467.6	467.6

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Enthalpy (J/mol) of Saturated Carbon Dioxide

Table 2 Enthalpy (J/mol) of Saturated Carbon Dioxide

Temp (°C)	Press (bar)	Liquid	Vapour	Vaporization	Temp (°C)	Press (bar)	Liquid	Vapour	Vaporization
–20	19.70	–15506	–3075.8	12430	9	43.92	–12488	–3646.8	8841.7
–19	20.31	–15411	–3079.5	12332	10	45.02	–12369	–3692.2	8676.7
–18	20.94	–15316	–3084.1	12232	11	46.15	–12248	–3740.6	8507.1
–17	21.58	–15220	–3089.5	12130	12	47.30	–12124	–3792.0	8332.5
–16	22.24	–15123	–3095.8	12028	13	48.47	–11999	–3846.7	8152.4
–15	22.91	–15027	–3102.9	11924	14	49.66	–11872	–3905.0	7966.5
–14	23.59	–14929	–3111.0	11818	15	50.87	–11741	–3967.2	7774.2
–13	24.29	–14831	–3120.0	11711	16	52.11	–11609	–4033.8	7574.8
–12	25.01	–14733	–3130.0	11603	17	53.37	–11473	–4105.0	7367.5
–11	25.74	–14634	–3141.0	11493	18	54.65	–11333	–4181.6	7151.6
–10	26.49	–14535	–3153.1	11382	19	55.96	–11190	–4264.1	6926.0
–9	27.25	–14435	–3166.2	11268	20	57.29	–11043	–4353.2	6689.4
–8	28.03	–14334	–3180.4	11153	21	58.65	–10890	–4450.0	6440.1
–7	28.82	–14232	–3195.8	11037	22	60.03	–10732	–4555.7	6176.2
–6	29.63	–14130	–3212.3	10918	23	61.44	–10567	–4671.8	5895.1
–5	30.46	–14027	–3230.2	10797	24	62.88	–10394	–4800.4	5593.2
–4	31.30	–13924	–3249.3	10675	25	64.34	–10210	–4944.5	5265.5
–3	32.16	–13820	–3269.7	10550	26	65.84	–10013	–5108.3	4904.9
–2	33.04	–13714	–3291.6	10423	27	67.36	–9798.2	–5298.5	4499.7
–1	33.94	–13608	–3314.9	10293	28	68.92	–9557.1	–5526.7	4030.4
0	34.85	–13501	–3339.8	10162	29	70.51	–9273.2	–5816.6	3456.6
1	35.78	–13393	–3366.2	10027	29.5	71.32	–9103.6	–6001.2	3102.4

Table 2 Enthalpy (J/mol) of Saturated Carbon Dioxide (cont.)

Temp (°C)	Press (bar)	Liquid	Vapour	Vaporization	Temp (°C)	Press (bar)	Liquid	Vapour	Vaporization
2	36.73	–13285	–3394.4	9890.2	30.0	72.14	–8899.9	–6234.0	2665.9
3	37.70	–13175	–3424.3	9750.2	30.2	72.47	–8802.4	–6349.6	2452.8
4	38.69	–13063	–3456.0	9607.4	30.4	72.80	–8689.6	–6486.6	2203.0
5	39.70	–12951	–3489.8	9461.4	30.6	73.13	–8551.4	–6658.5	1892.9
6	40.72	–12838	–3525.6	9312.0	30.8	73.47	–8359.4	–6903.6	1455.8
7	41.77	–12723	–3563.6	9159.1	30.97	73.77	–7905.2	–7464.6	440.6
8	42.83	–12606	–3603.9	9002.4	30.98	73.77	–7818.4	–7818.4	0.000

3

Entropy (J/mol•K) of Saturated Carbon Dioxide

Table 3 Entropy (J/mol•K) of Saturated Carbon Dioxide

Temp (°C)	Press (bar)	Liquid	Vapour	Vaporization	Temp (°C)	Press (bar)	Liquid	Vapour	Vaporization
–20	19.70	–83.89	–34.79	49.10	9	43.92	–73.05	–41.71	31.34
–19	20.31	–83.53	–35.01	48.52	10	45.02	–72.64	–42.00	30.64
–18	20.94	–83.16	–35.22	47.94	11	46.15	–72.24	–42.30	29.94
–17	21.58	–82.80	–35.44	47.36	12	47.30	–71.82	–42.60	29.22
–16	22.24	–82.43	–35.66	46.77	13	48.47	–71.41	–42.92	28.49
–15	22.91	–82.07	–35.88	46.19	14	49.66	–70.98	–43.24	27.74
–14	23.59	–81.70	–36.10	45.60	15	50.87	–70.55	–43.57	26.98
–13	24.29	–81.34	–36.32	45.02	16	52.11	–70.12	–43.92	26.20
–12	25.01	–80.97	–36.54	44.43	17	53.37	–69.67	–44.28	25.39
–11	25.74	–80.61	–36.77	43.84	18	54.65	–69.22	–44.65	24.56
–10	26.49	–80.24	–36.99	43.25	19	55.96	–68.75	–45.04	23.71
–9	27.25	–79.88	–37.22	42.66	20	57.29	–68.27	–45.45	22.82
–8	28.03	–79.51	–37.44	42.06	21	58.65	–67.78	–45.88	21.89
–7	28.82	–79.14	–37.67	41.47	22	60.03	–67.27	–46.34	20.93
–6	29.63	–78.77	–37.90	40.87	23	61.44	–66.74	–46.83	19.91
–5	30.46	–78.40	–38.14	40.27	24	62.88	–66.18	–47.36	18.82
–4	31.30	–78.03	–38.37	39.66	25	64.34	–65.60	–47.94	17.66
–3	32.16	–77.66	–38.61	39.05	26	65.84	–64.97	–48.57	16.40
–2	33.04	–77.28	–38.85	38.44	27	67.36	–64.29	–49.29	14.99
–1	33.94	–76.91	–39.09	37.82	28	68.92	–63.52	–50.13	13.38
0	34.85	–76.53	–39.33	37.20	29	70.51	–62.61	–51.17	11.44
1	35.78	–76.16	–39.58	36.58	29.5	71.32	–62.07	–51.82	10.25

Table 3 Entropy (J/mol•K) of Saturated Carbon Dioxide (cont.)

Temp (°C)	Press (bar)	Liquid	Vapour	Vaporization	Temp (°C)	Press (bar)	Liquid	Vapour	Vaporization
2	36.73	–75.78	–39.83	35.94	30.0	72.14	–61.42	–52.62	8.794
3	37.70	–75.39	–40.09	35.31	30.2	72.47	–61.10	–53.02	8.086
4	38.69	–75.01	–40.34	34.66	30.4	72.80	–60.74	–53.48	7.257
5	39.70	–74.62	–40.61	34.02	30.6	73.13	–60.29	–54.06	6.232
6	40.72	–74.23	–40.87	33.36	30.8	73.47	–59.67	–54.88	4.790
7	41.77	–73.84	–41.15	32.69	30.97	73.77	–58.19	–56.74	1.449
8	42.83	–73.45	–41.43	32.02	30.98	73.77	–57.90	–57.90	0.000